CONTAMINATION OF THE SULPHUR RIVER WILDLIFE MANAGEMENT AREA AND WATERSHED IN AND NEAR TEXARKANA, ARKANSAS AND TEXAS

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Abstract

The U.S. Fish and Wildlife Service conducted this study in response to the concern of local citizens that contaminants from four industrial facilities (two of which are superfund sites) and a sanitary landfill were adversely affecting fish and wildlife resources in the Sulphur River Wildlife Management Area (WMA) and adjacent watershed in and near Texarkana, Arkansas and Texas. Concentrations of organochlorines (DDT and associated metabolites and polychlorinated biphenyls), polycyclic aromatic hydrocarbons (PAHs), dioxins and metals (mercury, chromium, lead, nickel, selenium, and zinc) were detected in sediment and fish samples at levels sufficient to pose a threat to fish and wildlife resources. Microtox bioassays indicated that pore water samples from sediments in Days, Wagner and Nix Creeks, all of which are upstream from the WMA, were toxic. The primary sources of PAH contamination, mercury, PCBs and dioxin appeared to be one of the superfund sites (Koppers), a paper pulp mill, and an operational wood treatment plant, respectively. Additional contaminant sources were suspected, but identification of these sources was beyond the scope of this study. Several recommendations are made for additional studies to investigate the need, feasibility, and responsibility for reduction, cleanup, and monitoring of contaminants of concern.

Key words: organochlorine pesticides, polychlorinated biphenyls, polycyclic aromatic hydrocarbons, DDT, DDE, mercury, contamination, fish, sediments, paper mills, wood treatment, landfill

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Introduction

In 1989, members of a local citizens organization [Friends United for a Safe Environment (FUSE)] in Texarkana, Arkansas and Texas were concerned that contaminants from four industrial facilities (including the Koppers and Texarkana Wood Preservative superfund sites) and a sanitary landfill were adversely affecting fish and wildlife resources in the Texarkana area. FUSE was particularly concerned about the Sulphur River Wildlife Management Area (WMA; Fig. 1) which is downstream of all five facilities. Thus, the Fish and Wildlife Service (Service) was requested to conduct a study to investigate and document contaminant impacts in the Sulphur River watershed, including the WMA.

The purpose of this study was threefold: (1) to determine the levels of contaminants in sediments, water, and fish from areas near each facility; (2) to determine whether discharges from any or all of the facilities resulted in adverse impacts to fish and wildlife resources in general; and, more specifically, (3) to determine whether discharges from any or all of the five facilities resulted in adverse impacts to the WMA.

Site Description

Sulphur River Wildlife Management Area

The 6,475 ha WMA (Fig. 1) was established as a Federal Aid Project in the early 1960's. Located in Miller County, Arkansas east of the Texas border and approximately 17 km south of Texarkana, Arkansas and Texas, the WMA averages 3.2 km in width and extends along the Sulphur River for approximately 32 km. Current land use includes 5,763 ha of forested land, 453 ha of lakes and streams, and 259 ha of open land.

The WMA provides excellent habitat for migratory waterfowl including the wood duck (*Aix sponsa*) mallard (*Anas platyrhynchos*), green-winged teal (*A. crecca*), and gadwall (*A. strepera*). Other avian, mammalian, and piscine species that commonly occur on the WMA include the great blue heron (*Ardea herodias*), green-backed heron (*Butorides striatus*), great egret (*Casmerodius albus*), little blue heron (*Egretta caerulea*), cattle egret (*Bubulcus ibis*), various passerines and shorebirds, eastern wild turkey (*Meleagris gallopavo*), white-tailed deer (*Odocoileus virginianus*), raccoon (*Procyon lotor*), largemouth bass (*Micropterus salmoides*), channel catfish (*Ictalurus punctatus*), bowfin (*Amia calva*), spotted gar (*Lepisosteus oculatus*), yellow bullhead (*Ameiurus natalis*), and bluegill (*Lepomis macrochirus*). In addition, the endangered southern bald eagle (*Haliaeetus leucocephalus*) overwinters on the WMA.

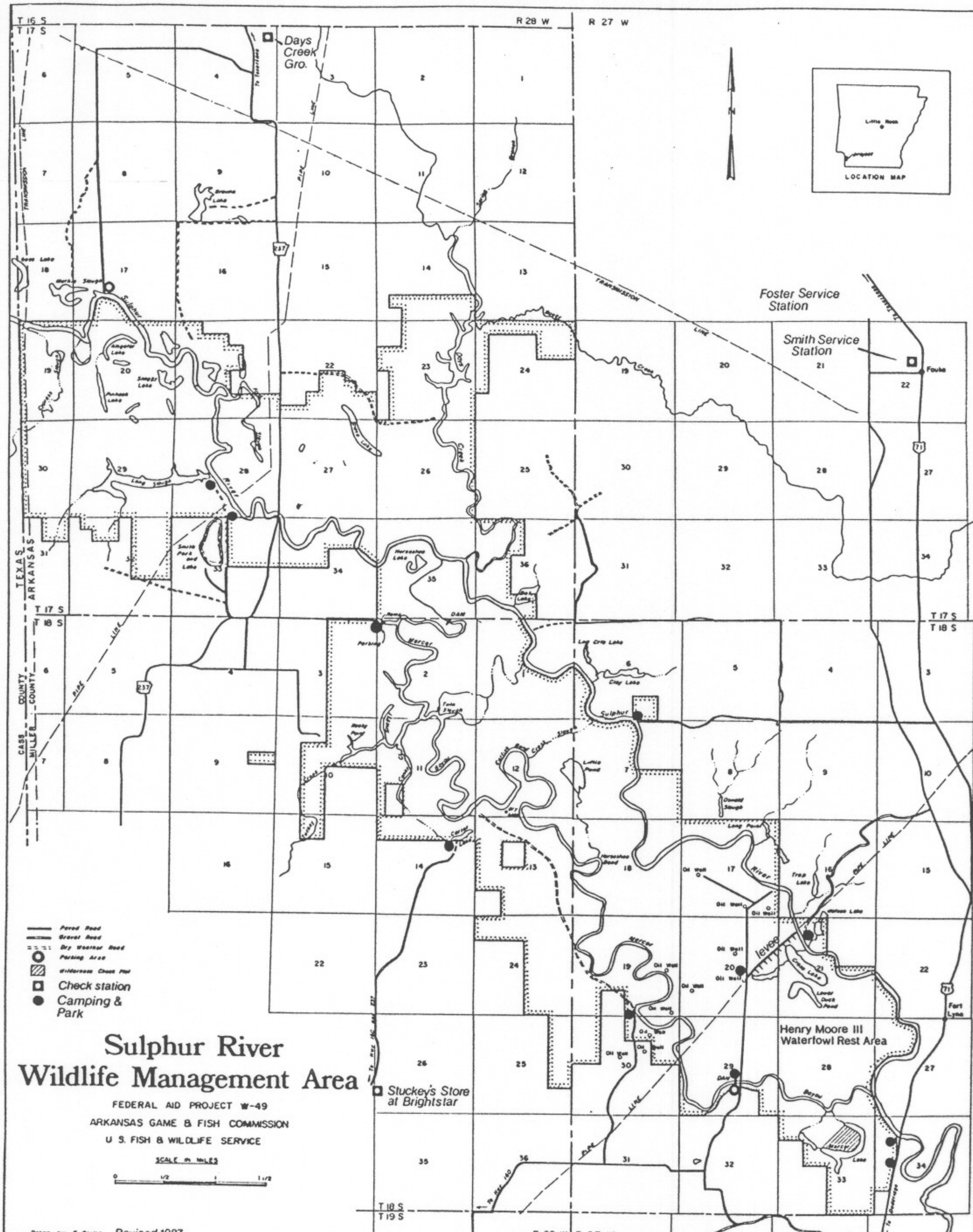

Figure 1. Sulphur River Wildlife Management Area

Suspected Contaminant Sources

Koppers Superfund Site

The Koppers facility is located on the 100 year floodplain of Wagner Creek, Texarkana, Texas (Fig. 2). The 25 ha site, formerly a wood treatment facility, began operations in 1910. Chemicals used in the treatment process included pentachlorophenol (PCP), creosote, and various metallic salts. After operations ceased in 1961, the structures were removed, and the property was sold for residential and industrial development.

Carver Terrace, Incorporated purchased 13.8 ha at the north end of the site (Carver Terrace Subdivision) in 1964 and subsequently constructed 79 homes. In 1975, Mount Zion First Missionary Baptist Church purchased 0.2 ha on the southeast corner of the subdivision and built a church. The remaining land (11.2 ha) was sold to the Kennedy Sand and Gravel Company, which mined sand and gravel from the late 1970's to 1984.

In 1980, the state of Texas found that the soils and ground water were contaminated with PCP, polycyclic aromatic hydrocarbons (PAHs), and trace metals (U.S. Environmental Protection Agency 1992). As a result, the U.S. Environmental Protection Agency (EPA) placed the Koppers facility on the National Priorities List. Funds have been allocated to purchase the homes located on the site and to provide relocation assistance to the residents. Once the buyout is completed, all buildings will be demolished or removed (U.S. Environmental Protection Agency 1992).

Texarkana Wood Preservative

The 10.1 ha Texarkana Wood Preservative site is located in the floodplain of Nix Creek, Texarkana, Texas (Fig. 2). The facility began operations in 1961 and closed in July 1984. Creosote and PCP were used in the treatment process. While operational, Texarkana Wood Preservative was issued three citations by the Texas Water Commission for unauthorized discharges of process waste water. Presently, the site consists of abandoned buildings, equipment, five waste water holding ponds, and numerous barrels of unknown contents.

Preliminary sampling indicated that waste water, sludges, and soils were contaminated with PCP, various dioxin and furan congeners, and PAHs (U.S. Environmental Protection Agency 1992). In 1986, EPA placed the site on the National Priorities List for cleanup.

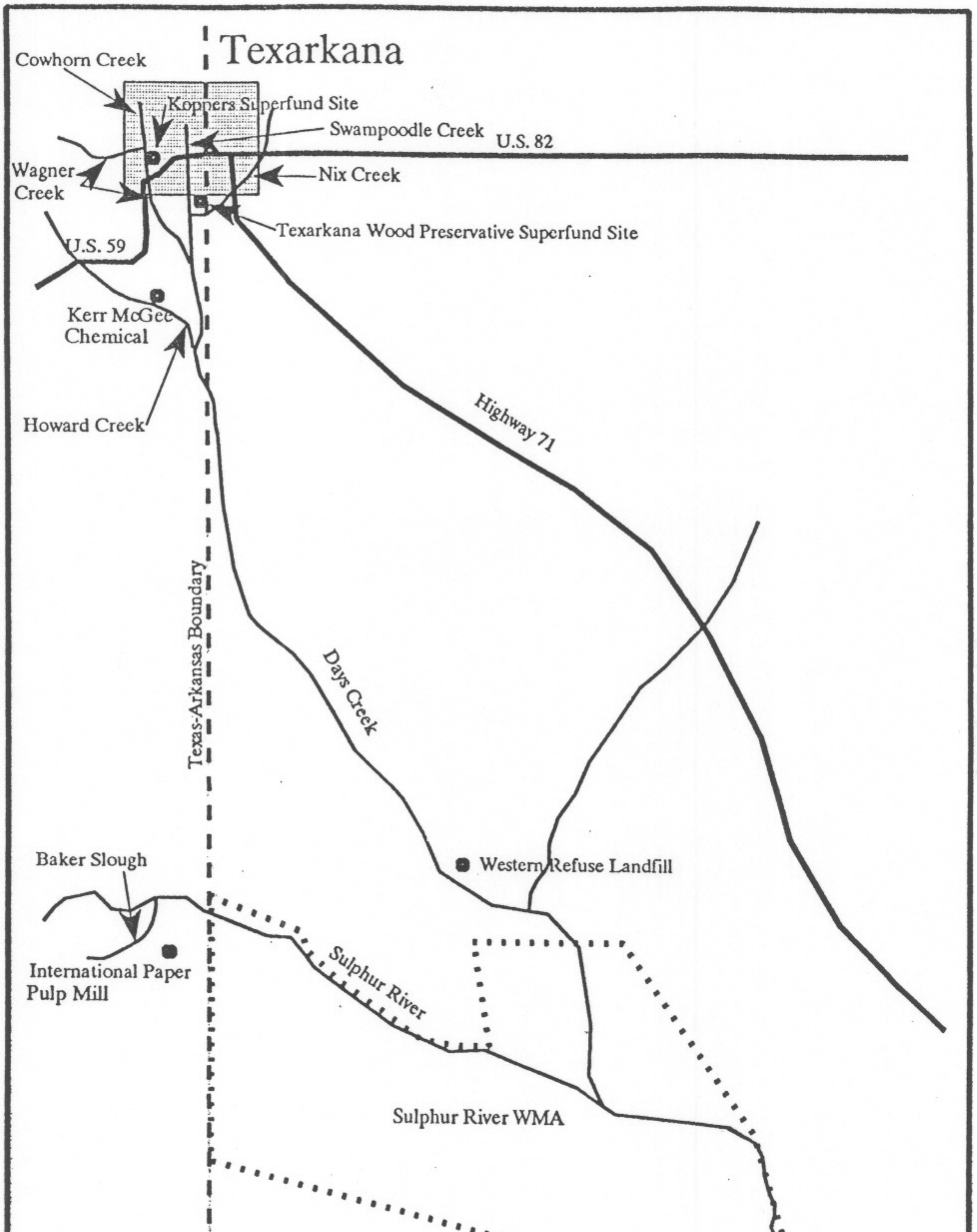

Figure 2. Location of superfund sites, operational wood treatment plant, landfill, and paper mill in the watershed of the Sulphur River Wildlife Management Area.

Kerr-McGee Chemical

Kerr McGee Chemical wood treatment plant is located near the confluence of Howard and Nix Creeks south of Texarkana, Texas (Fig. 2). The 97-ha facility, which produces railroad crossties, is reputed to be the largest operational wood treatment facility in the United States. A large holding pond used to collect process waste water is located at the north end of the site, adjacent to Nix Creek.

Western Refuse Landfill

The Western Refuse Landfill, operated by Western Waste Industries, occupies a 32.4-ha tract located approximately 2.5 km east of Highway 237 about 16 km south of Texarkana, Arkansas (Fig. 2). Landfill operations, which began in 1976, filled the northern half (16.2 ha) of the tract by 1982. Records regarding construction, or of the types and volumes of wastes deposited in this portion of the landfill have not been found. The southern half of the tract is designed for sectorized filling with a 1.2-1.8 m clay bottom liner and a 0.6 m clay sidewall liner. The landfill currently accepts approximately 360 tons of industrial and municipal refuse per day, including an average of 13.5 t of asbestos. Limited sampling of surface soils indicated that the site was contaminated with metals, PAHs, and other volatile organic contaminants (Wilkening 1991).

International Paper Pulp Mill

The International Paper pulp mill is located on Baker Slough, a tributary of the Sulphur River, approximately 3 km upstream from the western boundary of the WMA. Chlorine, used in the bleaching process, converts brown pulp to white pulp. This process typically creates large quantities of environmental contaminants including dioxins, furans, and metals (Eisler 1987b, Cherwinsky and Murray 1988).

Methods

In March and August 1990, we collected water and sediment samples from 39 sites in the study area. The location and description of each site is presented in Figure 3 and Table 1, respectively. Water and sediments were collected from sites 1 through 11 in March 1990. In August 1990, we collected samples from sites 12 through 39.

Water samples were collected with a Kemmerer sampler or by direct immersion of a sample bottle. As a result of drought conditions in August 1990,

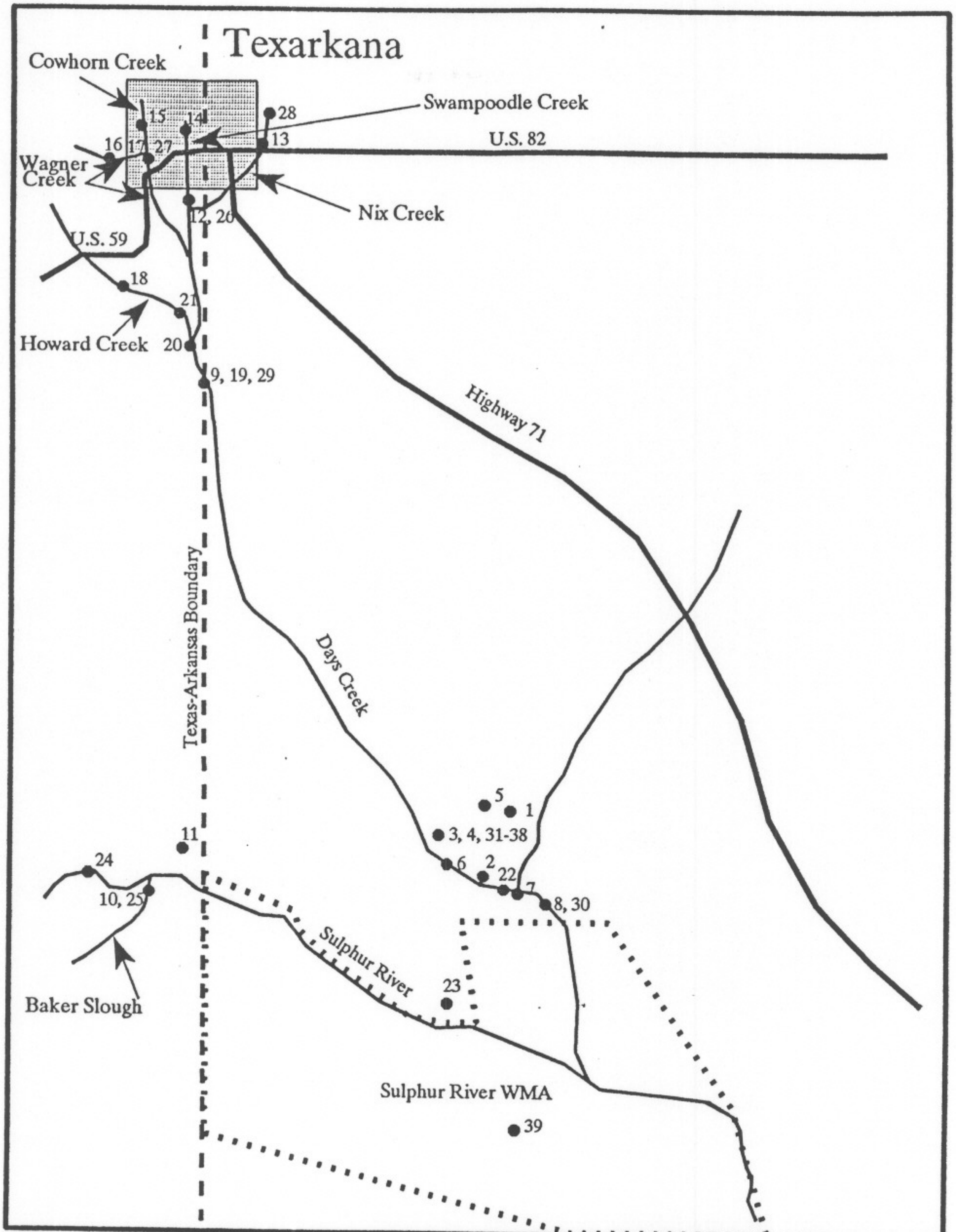

Figure 3. Locations of sampling sites on the Sulphur River Wildlife Management Area, March and August 1990 and July 1991.

Table 1. Sampling sites for collection of water (W), sediments (S) and fish (F) from the Sulphur River watershed in and near Texarkana, Arkansas and Texas.

Site	Media Collected	Location
1	WS	Settling ponds behind Fina Oil adjacent to Days Creek
2	WS	Days Creek behind Fina Oil
3	WS	Standing pool at north end of landfill
4	WS	Unnamed creek at north end of landfill
5	WS	McCullum Pond
6	WS	Days Creek at Highway 237 bridge
7	WS	Four Mile Creek adjacent to abandoned landfill
8	WS	Drainage from abandoned landfill
9	WS	Days Creek at Stateline bridge
10	WS	Bakers Slough below International Paper effluent outfall
11	WS	Goss Lake
12	WSF	Days Creek below Texarkana Wood Preservative site
13	WSF	Nix Creek at 12th Street bridge
14	WS	Swamppoodle Creek at Richmond Road
15	WS	Cowhorn Creek at Tucker Creek
16	WS	Wagner Creek at Highway 67 bridge
17	WS	Wagner Creek at Jameson Road below Koppers site
18	WS	Howard Creek at Highway 558 bridge
19	WS	Days Creek at Stateline Bridge (same as 9)
20	WS	Days Creek below Kerr-McGee facility
21	WS	Howard Creek immediately upstream from confluence with Days Creek

Table 1 continued.

Site		Location
22	WSF	Large ditch at Highway 237 bridge below Fina Oil
23	WS	Sulphur River at Highway 237 bridge
24	WS	Sulphur River adjacent to International Paper levee
25	WSF	Bakers Slough below International Paper effluent outfall (same as 10)
26	WS	Days Creek below Texarkana Wood Preservative site (same as 12)
27	WS	Wagner Creek adjacent to Koppers site
28	WSF	Nix Creek at 18th Street bridge
29	WSF	Days Creek along Stateline Road by culverts
30	WS	Days Creek below confluence with Four Mile Creek
31	WS	North end of industrial landfill near creek bed
32	WS	North end of industrial landfill beside fence
33	WS	Area where runoff pools at north end of landfill
34	WS	East side of landfill just inside fence line
35	WS	Drainage ditch on south side of landfill
36	WS	Drainage pools on south side of landfill
37	WS	Artesian well on south side of landfill
38	WS	Artesian well ponds on south side of landfill
39	WSF	Mercer Bayou where the Sulphur River enters the bayou during high flow

we collected surface water samples at only those locations where large pools or flowing water were present.

Sediment samples were collected with a petite ponar dredge, an Eckman dredge, or a stainless steel spoon. Water and sediment samples were placed in chemically-cleaned jars, and stored in wet ice until frozen.

Fish (Table 2) were collected in July 1991 using a battery-operated backpack electroshocker on smaller streams and with a direct-current boom-electrofishing boat on larger streams. All fish were weighed, measured, wrapped in aluminum foil, and packed in ice until frozen. With the exception of bowfin and spotted gar tissues from Mercer Bayou on the WMA (site 39), all fish samples were composites consisting of two to 19 fish (Table 2). The bowfin and the spotted gar samples from Mercer Bayou contained one fish each.

Microtox™ bioassays, using the 100% procedure (Microbics 1990), were completed on selected surface water samples and pore water extracts from sediment samples to determine toxicity. A control sample of sterile, nontoxic diluent was also included with the four dilutions of the original sample. Five and 15 minute tests were completed to determine organic and inorganic toxicity, respectively. Positive and negative blanks using phenol and distilled water were analyzed periodically to assure procedural accuracy. Toxicity was indicated when light transmittance from the photobacterium (*Photobacterium phosphoreum*) was inhibited. The effective concentration (EC_{50}), based on percentage of the original sample which caused a 50% reduction in light transmittance, was calculated for each sample. Toxicity units (TUs; $=100/EC_{50}$) were calculated and the relative toxicity of each sample was derived using methodology developed by Smith (1991) (Table 3).

Residue analysis for organochlorines (OCs), PAHs and metals were conducted for sediment samples indicated to be toxic by Microtox™ bioassay of the pore water. Following initial residue analysis, eight sediment samples were selected for a homologue scan of dioxins and furans. All fish tissues were analyzed for OCs, PAHs, and metals. Four fish samples were selected for dioxin and furan analyses.

All residue analyses, with the exception of the homologue scan for dioxins and furan, were performed by contract laboratories through the Services's Patuxent Analytical Control Facility. Dioxin and furan analyses were completed by the National Fisheries Contaminant Research Center, Columbia, Missouri.

Acceptable performance (recovery variation <20% for all chemicals detected) on spikes, blanks, and duplicates was documented in laboratory quality control reports.

Organochlorine, PAH, metal, and dioxin (or equivalent) concentrations were compared to various concern levels for these compounds (Table 4). Contaminant concentrations that equalled or exceeded concern levels were considered elevated.

Statistical comparisons of Microtox™ toxicity and contaminant concentrations in sediments were conducted using step-wise multiple linear

Table 2. Fish samples from the Sulphur River watershed - July 1991.

Site[a]	Species	*n*	Sample Weight (g)	Analyses Requested[b,c]
12	Green sunfish *(Lepomis cyanellus)*	2	104	A
13	Sunfish *(Lepomis* spp.*)*[d]	8	167	A
22	Yellow bullhead *(Ictalurus natalis)*	4	255	A
25	Largemouth bass *(Micropterus salmoides)*	4	1,786	B
25	Spotted gar *(Lepisosteus oculatus)*	4	4,585	A
25	Channel catfish *(Ictalurus punctatus)*	6	492	B
28	Yellow bullhead	6	422	A
29	Yellow bullhead	19	94	A
39	Bowfin *(Amia calva)*	1	1,462	B
39	Spotted gar	1	643	B

[a]See Figure 2.
[b]A=organochlorines, polynuclear aromatic hydrocarbons and metals; B=all the above plus dioxins and furans.
[c]When $n>1$, sample composited.
[d]Sample consisted of one *L. macrochirus*, two *L. megalotis* and five *L. cyanellus.*

Table 3. Relative toxicity of Microtox^{TM} values based on EC_{50} value (% concentration of sample) and toxicity units ($100/EC_{50}$).

EC_{50} Value (%)	Toxicity Units	Relative Toxicity
100 - 80	1.0 - 1.2	Slightly toxic
79 - 60	1.3 - 1.7	Moderately toxic
59 - 40	1.8 - 2.5	Toxic
39 - 20	2.6 - 5.0	Very toxic
≤19	>5.0	Extremely toxic

Table 4. Food and Drug Administration (FDA) action limits, predator protection limits (PPL) and other levels of concern for organic and inorganic compounds detected in fish and sediment samples collected from the Sulphur River watershed. Concentrations are ppm wet weight for fish tissues and ppm dry weight for sediments.

	Matrix		
Compound	Fish Tissue	Sediments	Reference
trans-nonachlor	0.3 (FDA)		Kimbrough and Scheuplein (1988)
	<0.1 (NOEL)[a]		Eisler (1990)
Polychlorinated biphenyls (PCBs)	2.0 (FDA)		Kimbrough and Scheuplein (1988)
	<0.1 (PPL)		Eisler (1986a)
		0.0029 (SLC)[b]	Long and Morgan (1990)
Dieldrin	0.3 (FDA)		Kimbrough and Scheuplein (1988)
	0.1 (PPL)		Fyfe et al. (1976)
		0.02 (ER-L)[c]	Long and Morgan (1990)
p-p'-DDD	(see DDTM)	0.002 (ER-L)	Long and Morgan (1990)
p,p'-DDE	(see DDTM)	0.002 (ER-L)	Long and Morgan (1990)
p,p'-DDT	(see DDTM)	0.001 (ER-L)	Long and Morgan (1990)
DDTM[d]	5.0 (FDA)		Kimbrough and Scheuplein (1988)
	1.0 (PPL)		U.S. Environmental Protection Agency (1972)
		0.0006	Bolton et al. (1985)
		0.003 (ER-L)	Long and Morgan (1990)
Polycyclic aromatic hydrocarbons (PAHs)			
Total PAHs	<0.0001 (PPL)		Eisler (1987a)
		4.0[e] (ER-L)	Long and Morgan (1990)

Table 4 continued.

	Matrix		
Compound	Fish Tissue	Sediments	Reference
2,3,7,8-TCDD[f]	0.00002 (FDA)		Eisler (1986b)
	0.000012 (PPL)	Eisler (1986b)	
2,3,7,8-TCDF[g]	0.0002 (FDA)		Smith et al. (1990)
	0.00012 (PPL)		Smith et al. (1990)
Arsenic	0.5 (PPL)		Walsh et al. (1977)
		33.0 (ER-L)	Long and Morgan (1990)
Cadmium	0.5 (PPL)		Walsh et al. (1977)
		5.0 (ER-L)	Long and Morgan (1990)
Chromium	0.2 (PPL)		Eisler (1986c), Schmitt and Finger (1987)
		80.0 (ER-L)	Long and Morgan (1990)
Copper		70.0 (ER-L)	Long and Morgan (1990)
Lead	0.3[h]		Schmitt and Finger (1987), Eisler (1988a)
	0.3 (PPL)		Eisler (1988a)
		35.0 (ER-L)	Long and Morgan (1990)
Mercury	1.0 (FDA)		Kimbrough and Scheuplein (1988)
	0.1 (PPL)		Eisler (1987b)
		0.15 (ER-L)	Long and Morgan (1990)
Nickel		30.0 (ER-L)	Long and Morgan (1990)
Selenium	1.0[i]		Irwin (1991)
	0.5 (PPL)		Walsh et al. (1977)

Table 4 continued.

	Matrix		
Compound	Fish Tissue	Sediments	Reference
Vanadium	0.5 (PPL)		Irwin (1991)
Zinc	<178 (dry weight)[j]		Eisler (1993)
		<50.0	U.S Fish and Wildlife Service (1992)
		120.0 (ER-L)	Long and Morgan (1990)

[a]No Observed Effect Level.
[b]Screening level concentration for freshwater; i.e., that concentration at which, based on a National average, 95 percent of the infauna are present.
[c]Effects Range-Low; i.e., the level at which effects on biota were first observed.
[d]Total DDT; i.e., DDT plus metabolites (DDD and DDE).
[e]ER-Ls for individual PAHs vary from 35 ppb (fluorene) to 600 ppb (fluoranthene).
[f]2,3,7,8-tetrachlorodibenzo-*p*-dioxin.
[g]2,3,7,8-tetrachlorodibenzo-*p*-furan.
[h]California Department of Health limit; no FDA limit established.
[i]Edible tissue guideline; no FDA limit.
[j]No predator protection limit established; however, bird diets containing in excess of 178 ppm dry weight result in various sublethal effects.

regression (for all analytes) and, for each analyte, Pearson's product moment correlation (SAS Institute, Inc. 1985).

Results and Discussion

Microtox™ *Analyses*

Analyses of those surface water samples collected in March 1990 indicated that only two, water from the standing pool at the north end of the Western Refuse landfill (site 3) and water from Days Creek at the Stateline bridge (site 9), were toxic (Table 5). Whereas the source of the contaminant causing toxicity of surface water at site 3 is evident, the toxic conditions observed at site 9 could have originated from any one of a number of sources, including Kerr-Mcgee, Koppers, Texarkana Wood Preservative, and highway runoff. None of the surface water samples analyzed from August 1990 collections demonstrated toxicity.

Of 39 pore water samples extracted from sediments collected in March and August 1990, only seven were toxic (Table 5). Four of these were adjacent to the Western Refuse landfill (sites 31, 33, 36 and 38), two (sites 9 and 19) were from sediments collected in Days Creek at the Stateline Bridge in March and August 1990, respectively. The remaining sample was collected in Wagner Creek adjacent to the Koppers site (site 27). The source of toxicity of sediments collected at the Stateline Bridge cannot be determined from the data. Pore water extracts from sediments collected at downstream of Kerr-McGee Chemical (sites 20 and 21) were not toxic. The same was true for pore water extracts from sediments collected downstream of the Texarkana Wood Preservative site (sites 12 and 26) and at site 17 below the Koppers site. Even though these mentioned facilities do not directly appear to be responsible for the toxic sediments, the sediments in question were collected from backwater areas where deposition of potentially toxic particulate matter may be responsible for the values noted. Samples collected adjacent to the sanitary landfill and to Koppers Superfund site showed that these facilities were the toxic sources.

Statistical analyses to determine if toxicity, as measured by Microtox™ bioassay, was correlated with residue concentrations, either collectively or individually, did not yield verification. Step-wise multiple regression, which would intuitively seem to be the proper test given that the bacteria were subjected to a complex mixture of contaminants rather than a single element or compound, indicated little or no correlation. When each contaminant was considered separately, only aluminum (Al) showed a significant correlation (r=-0.942, p=0.002). Lead (r=-0.655, p=0.11) and zinc (r=-0.731, p=0.062) correlations, although not significant ($\alpha<0.05$), indicative a correlative effect.

Table 5. Microtox^{TM} bioassay results[a] for surface (SW) and pore water (PW) samples collected from the Sulphur River watershed in March (Sites 1-11) and August (Sites 12-39), 1990.

Sample No.	Time (min)	EC_{50} (%)	Toxicity Units[b]
SW03	5	36	2.8
	15	35	2.9
SW09	5	18	5.6
	15	18	5.6
PW09	5	11	9.1
PW19	5	NT[c]	
	15	89	1.1
PW27	5	34	2.9
	15	36	2.8
PW31	5	37	2.7
	15	37	2.7
PW33	5	17	5.9
	15	19	5.3
PW36	5	26	3.9
	15	32	3.1
PW38	5	97	1.0
	15	98	1.0

[a]Results are only presented for those samples which were toxic.
[b]Toxicity Units=100/EC_{50}.
[c]Not toxic.

Organochlorines

Only two OC compounds were above the detection limit (0.01 ppm dry weight) in sediments: DDE was detected at a concentration of 0.02 ppm in the sample from the artesian well ponds south of the Western Refuse landfill (site 38); and PCBs at a level of 0.16 ppm in sediments taken from the north end of the landfill (site 32). Both were above the respective concern levels for sediments (Table 4).

All fish tissue samples contained one or more OC compounds (Table 6); however, the only compound present in all samples was *p,p'*-DDE. *p,p'*-DDE concentrations were above, or slightly below, the recommended predator protection limit (DDTM=1.0 ppm wet weight) in spotted gar (*Lepisosteus oculatus*) tissues from Baker Slough (site 25) and Mercer Bayou (site 39). However, since spotted gar were collected only at these two locations, we cannot be sure whether these results are indicative of high levels of *p,p'*-DDE in the environment, or merely reflect interspecific differences in bioaccumulation. It should be noted that the mean concentration of DDT plus metabolites (DDTM) in fish samples collected throughout the United States was only 0.26 parts per million (ppm; Schmitt and Brumbaugh 1990). Both spotted gar samples also exceeded this value.

Polychlorinated biphenyls were present in five of the ten fish samples (Table 6): sunfish (*Lepomis* spp.) and yellow bullhead (*Ictalurus natalis*) from Nix Creek (sites 13 and 28, respectively); yellow bullhead from Days Creek below the Western Refuse landfill (site 22); and spotted gar and channel catfish (*I. punctatus*) from Baker Slough below International Paper (site 25). Concentrations ranged from 0.2 ppm wet weight (ww; the limit of detection) to 1.21 ppm ww and were all greater than the recommended PPL of <0.1 ppm ww (Table 4).

The remaining OCs detected (*trans*-nonachlor, dieldrin, *p,p'*-DDD and *p,p'*-DDT; Table 6) were all below recommended PPLs and Food and Drug Administration (FDA) guidelines (Table 4).

Although exposure to any of these compounds may result in injury to fish and wildlife resources, PCBs are of greatest overall concern in the Sulphur River watershed as they are considered to be the most hazardous group of chemicals typically found in fish (Passino and Smith 1987). As polychlorinated biphenyls are lipophilic, the greatest concentrations are found in the highest trophic levels in the food chain. Thus, top predators such as largemouth bass, fish-eating mammals and birds, and perhaps the human population are at greatest risk.

Birds of prey exposed to PCBs have exhibited adverse effects on the endocrine system, particularly those hormones which regulate reproductive processes (Lincer and Peakall 1970). Other investigators have reported decreased

Table 6. Organochlorine concentrations (ppm wet weight) in fish collected from the Sulphur River watershed - July 1991.

	Sample Identification[a]									
Analyte	SF12	SF13	YB22	LB25	SG25	CC25	YB28	YB29	BF39	SG39
trans-nonachlor	0.02	0.05	-[b]	-	-	-	0.02	-	-	-
Dieldrin	0.04	0.04	0.02	-	-	-	-	0.03	-	-
p-p'-DDE	0.11	0.07	0.02	0.06	1.21	0.05	0.02	0.02	0.04	0.81
p-p'-DDD	0.03	0.02	-	-	0.05	-	-	-	-	0.02
p-p'-DDT	-	0.03	-	-	0.02	-	-	-	-	-
Total PCBs	-	0.95	0.23	-	0.20	0.57	1.21	-	-	-

[a]Samples were identified by species and sampling site; i.e., SF12=sunfish (*Lepomis* sp.) collected at site 12 (Table 1). Species: SF=sunfish; YB=yellow bullhead (*Ameiurus natalis*); LB=largemouth bass (*Micropterus salmoides*); SG=spotted gar (*Lepisosteus oculatus*); CC=channel catfish (*Ictalurus punctatus*); BF=bowfin (*Amia calva*).
[b]Below limit of detection: 0.2 ppm for PCBs; 0.02 for all other compounds.

sperm counts (Bird et al. 1983), decreased reproductive success (Fyfe et al. 1976), and hatching failure (Newton and Bogan 1978).

In fish, impairment of testicular steroid hormone, increased steroid hormone metabolism in kidney and liver, impaired ovarian growth, and decreased vitellogenin (yolk protein) and estradiol production have resulted from PCB exposure (Reijnders and Brasseur 1992). Walker and Peterson (1992) and Munawar et al. (1984) reported that PCB exposure resulted in increased early life stage mortality and suppression of the immune system, respectively.

Potential sources for OC contamination in Days Creek and Baker Slough may be identified, but we did not suspect OCs to be present in Nix Creek, which originally was chosen as a reference site. At this time, we cannot offer a potential source for the contamination present at sites 13 and 28 in Nix Creek. However, it is probable that local populations of species sensitive to *p,p'*-DDE and PCBs have been, and are, adversely impacted by these contaminants.

Polycyclic aromatic hydrocarbons

Many PAHs and several associated breakdown products have been documented to be carcinogenic, teratogenic, and mutagenic (Eisler 1987a). In addition, metabolic transformation of PAHs into even more hazardous chemicals has been reported to occur in sediments, soils, and various species of fish and wildlife (Krahan et al. 1984, Eisler 1987a).

Polycyclic aromatic hydrocarbons were detected in all sediment and fish samples analyzed (Tables 7 and 8). Total PAHs and carcinogenic PAHs in sediment samples from sites adjacent to Koppers Superfund site (site 27) or near Stateline Bridge (sites 9, 19 and 29) were above the 1.0 ppm level known to: (1) induce tumors in brown bullhead populations (Eisler 1987a); (2) be correlated with elevated incidence of liver cancers in fish (Malins et al. 1985, Malins et al. 1987); and (3) be correlated with decreased quality of fisheries and elevated internal and external lesions (Smith et al. 1993).

Fish samples had total PAH concentrations which exceeded concern levels of 1.0 ppm ww (see Table 4) only at Stateline bridge (site 29) (see Table 8). Additional fish collections in Nix Creek were also slightly elevated.

Although concentrations in fish are usually low due to rapid metabolism of PAHs (Lawrence and Weber 1984), concentrations of all PAH compounds detected in fish tissues were above the PPL (Table 4), as the PPL was less than the detection limit (0.001 ppm). Higher weight PAHs include some of the most carcinogenic compounds known to man. Many PAHs and breakdown products of PAHs have been documented to be tumorigenic, teratogenic and mutagenic to fish and wildlife resources (Eisler 1987a), Metabolic transformation of PAHs to even more hazardous chemicals can also occur in sediments and soils and in various fish and wildlife species (Krahn et al. 1984, Eisler 1987a). PAHs also have been implicated with severe anomalies in fish populations; particularly brown bullhead

Table 7. Polycyclic aromatic hydrocarbon (PAH) concentrations (ppm dry weight) in sediments from the Sulphur River watershed - March or August, 1990 (see text).

	Sample Site														
Analyte	9	19	20	25	26	27	28	29	31	32	33	34	36	38	39
2-methylnaphthalene	0.88	0.12	0.77	0.53	0.08	1.7	0.12	0.65	0.55	0.45	0.20	0.28	0.62	0.43	0.24
1-methylnaphthalene	0.48	0.08	0.43	0.33	0.06	1.3	0.08	0.35	0.42	0.35	0.14	0.21	0.45	0.28	0.18
Biphenyl	0.29	0.03	0.29	0.03	0.01	1.1	0.01	0.16	0.03	0.02	0.01	0.02	0.04	0.03	0.01
2,6-dimethylnaphthalene	0.30	0.05	0.28	0.09	0.02	1.1	0.02	0.25	0.07	0.04	0.03	0.05	0.09	0.09	0.03
Acenaphthalene	0.12	0.05	0.15	0.01	0.01	0.71	-[a]	0.25	-	0.01	-	0.01	0.01	0.02	-
Acenaphthene	0.94	0.13	0.70	0.25	0.04	3.9	0.07	0.69	0.09	0.12	0.01	0.28	0.23	0.17	0.09
2,3,4-trimethylnaphthalene	0.12	0.03	0.10	0.04	0.01	0.71	0.01	0.12	0.02	0.02	0.01	0.02	0.03	0.04	0.01
Fluorene	1.5	0.18	1.6	0.15	0.07	8.9	0.06	0.96	0.11	0.06	0.04	0.09	0.16	0.11	0.07
Phenanthrene	6.6	0.88	7.0	0.13	0.06	51.0	0.26	3.8	0.20	0.05	0.04	0.06	0.12	0.11	0.07
Anthracene	0.92	0.16	0.72	0.01	0.01	8.3	0.05	0.62	0.01	-	-	-	0.01	-	-
1-methylphenanthrene	0.24	0.04	0.19	0.01	0.01	1.9	0.01	0.16	0.01	0.01	0.01	0.01	0.01	0.01	-
Fluoranthene	4.5	1.1	5.0	0.01	0.06	22.0	0.12	2.9	0.03	0.01	-	0.01	0.01	0.01	-
Pyrene	2.7	0.68	2.3	0.01	0.07	13.0	0.07	1.8	0.03	0.01	-	0.01	0.01	0.02	-

Table 7 continued.

Analyte	Sample Site 9	19	20	25	26	27	28	29	31	32	33	34	36	38	39
Benz(a)anthracene[b]	0.87	0.32	1.1	-	0.02	2.1	0.02	0.64	0.01	-	-	-	0.01	-	-
Chrysene[b]	0.90	0.31	1.1	-	0.03	2.5	0.02	0.93	0.02	-	-	-	0.01	0.01	-
Benzo(b)fluoranthene[b]	0.61	0.23	0.65	-	0.03	0.89	0.01	0.61	0.01	-	-	-	0.01	0.01	-
Benzo(k)fluoranthene	0.38	0.25	0.85	-	0.03	0.88	0.02	0.56	0.01	-	-	-	0.01	0.01	-
Benzo(e)pyrene	0.34	0.17	0.55	-	0.03	0.62	0.01	0.51	0.01	-	-	-	0.01	-	-
Benzo(a)pyrene[b]	0.49	0.23	0.55	-	0.03	0.69	0.02	0.54	-	-	-	-	0.01	-	-
Perylene	0.19	0.07	0.19	-	0.01	0.63	0.01	0.23	-	-	-	-	0.01	0.01	-
Indenopyrene[b]	0.33	0.16	0.51	-	0.04	0.06	0.02	0.27	0.01	-	-	-	0.01	0.01	-
Dibenzanthracene[b]	0.07	0.03	0.08	-	0.01	0.07	-	0.09	-	-	-	-	0.01	-	-
Benzo(g,h,i)perylene	0.23	0.11	0.35	-	0.03	0.06	0.01	0.26	-	-	-	-	0.01	0.01	-
Total Carcinogenic PAHs	3.27	1.28	3.99	-	0.16	6.31	0.07	3.08	0.05	-	-	-	0.06	0.03	-
TOTAL PAHs	24.89	5.62	25.95	2.27	0.91	125.42	1.18	18.06	2.94	2.45	1.00	1.65	3.09	2.13	1.17

[a]Below detection limit of 0.01 ppm.
[b]Carcinogenic.

Table 8. Polycyclic aromatic hydrocarbon (PAH) concentrations (ppb wet weight) in fish collected from the Sulphur River watershed - July 1991.

	Sample Identification[a]									
Analyte	SF12	SF13	YB22	LB25	SG25	CC25	YB28	YB29	BF39	SG39
2-methylnaphthalene	5	12	19	10	5	15	2	107	5	14
1-methylnaphthalene	4	18	11	6	3	9	3	72	3	8
Biphenyl	2	2	8	1	1	1	3	35	1	1
2,6-dimethylnaphthalene	4	7	10	3	1	3	2	36	2	3
Acenaphthalene	1	1	7	-[b]	-	1	2	16	-	1
Acenaphthene	13	9	80	1	1	1	155	372	-	1
2,3,4-trimethylnaphthalene	11	6	7	5	2	2	4	16	1	2
Fluorene	10	10	49	1	2	1	19	242	1	2
Phenanthrene	23	24	66	5	3	3	8	368	1	2
Anthracene	4	9	32	1	1	1	6	82	-	1
1-methylphenanthrene	1	2	2	3	2	1	2	7	1	1
Fluoranthene	6	5	61	3	1	2	3	234	1	1
Pyrene	4	2	23	2	1	2	2	112	1	1

Table 8 continued.

	Sample Identification[a]									
Analyte	SF12	SF13	YB22	LB25	SG25	CC25	YB28	YB29	BF39	SG39
Benz(a)anthracene[c]	-	-	2	1	1	-	-	17	-	-
Chrysene[c]	1	1	7	1	1	1	1	24	-	-
Benzo(b)fluoranthene[c]	-	-	-	-	-	-	-	6	-	-
Benzo(k)fluoranthene	-	-	1	-	-	-	-	6	-	-
Benzo(e)pyrene	-	-	1	-	-	-	-	5	-	-
Benzo(a)pyrene[c]	-	-	-	-	-	-	-	4	-	-
Perylene	-	-	-	-	-	-	1	2	-	-
Indenopyrene[c]	-	-	-	-	-	-	-	2	-	-
Dibenzanthracene[c]	-	-	-	-	-	-	-	1	-	-
Benzo(g,h,i)perylene	-	-	-	-	-	-	-	2	-	-
TOTAL PAHs	99	114	410	53	30	55	217	1890	20	50

[a]Sample identification consists of a species code followed by the collection site; e.g., SF12 indicates sunfish, site 12. Species codes: BF=bowfin; CC=channel catfish; LB=largemouth bass; SF=sunfish; SG=spotted gar; YB=yellow bullhead.
[b]Below detection limit of 1 ppb.
[c]Carcinogenic.

in the Great Lakes. Several laboratory experiments (Black 1983, Grady et al. 1991) and field collections (Baumann et al. 1982, 1987, 1991; Smith et al. 1993) indicating a strong correlation of elevated hepatic lesions and external abnormalities in the presence of PAHs in sediments. Adult benthic fish from the Texarkana area, particularly Nix Creek, Wagner Creek near Koppers Superfund site and Stateline bridge, need further investigation for possible evidence of internal and external abnormalities.

Eisler (1987a) recommended a maximum daily human intake of no more than 16 μg total PAHs. A person eating 113 g (4 oz.) of catfish daily from site 22, 28 or 29 would receive a dose of 46.5, 24.6 and 214.3 μg, respectively; an amount equal to 1.5 to 13.3 times the recommended daily intake.

Dioxin and furans

Concentrations of dioxin (2,3,7,8-tetrachlorodibenzo-*p*-dioxin; TCDD) and furan (2,3,7,8-tetrachlorodibenzofuran; TCDF) were above the limit of detection [0.1 parts per trillion (ppt)] in sediments at four locations: Baker Slough below the International Paper effluent outfall (site 25), Wagner creek adjacent to the Kopper's site (site 27), Nix Creek at the 28th Street bridge (site 28), and Mercer Bayou in the WMA (site 39). Concentrations at site 27 (TCDF) and 28 (TCDD) were only 2x and 4x the detection limit, respectively. However, at Baker Slough, TCDD and TCDF concentrations were 3.0 and 28 ppt, respectively. In sediments from Mercer Bayou, only TCDF (20.0 ppt) was detected. Thus, International Paper appeared to be the major source of TCDD and TCDF in system sediments.

Dioxin and furans were detected in all fish tissue samples (Table 9). Toxicity equivalent factors (TEF) have been used to identify the level of potential toxicity indicated by the presence of various dioxin and furan congeners identified in a homologue scan of tissue (Personal communication, T. Schwartz, NFCRC, Columbia, MO). The TEF uses 2,3,7,8-TCDD as a factor of 1.0; all other dioxins and furans are assigned a factor equating to their potential toxicity in comparison to 2,3,7,8-TCDD. TEFs range from 0.0001 for octa-dioxins and furans to 1.0 for 2,3,7,8-TCDD. Most dioxins and furans have a TEF of 0.1. TEF concentrations for all dioxins and furans ranging from 10 to 50 ppt are levels of concern. With the exception of Mercer Bayou (site 39), where a spotted gar had an elevated TEF of 21.6 ppt, dioxin and furan concentrations and their corresponding TEF were below concern levels in all fish tissue samples (Table 9).

Of 75 possible dioxin isomers, only TCDD has been studied extensively. TCDD is also the most toxic isomer for induction of enzyme activity (Bason and Colburn 1992). Eisler (1986b) noted that TCDD was the most toxic synthetic compound ever tested under laboratory conditions. A variety of adverse effects resulting from exposure to TCDD have been reported in the literature.

Walker and Peterson (1992) reported lake trout (*Salvelinus namaycush*) and rainbow trout (*Oncorhynchus nykiss*) sac fry mortality associated with yolk sac

Table 9. Dioxin and furan concentrations (ppt wet weight) in fish collected from the Sulphur River watershed - July 1991. Toxicity equivalent factor[a] (TEF) in ().

	Sample Identification[b]				
Analyte	YB22	LB25	CC25	BF39	SG39
2,3,7,8-TCDD[c]	0.53	2.2	4.3	1.7	17.0
2,3,7,8-TCDF[d]	0.4(0.04)	13.0(1.3)	3.3(0.33)	20.5(2.05)	35.0(3.5)
Total[e]	83.6(2.38)	29.5(3.63)	59.0(5.28)	35.4(4.26)	76.0(21.6)

[a]2,3,7,8-TCDD=1.0
[b]Sample identification consists of a species code followed by the collection site; e.g., LB25 indicates largemouth bass, site 25. Species codes: CC=channel catfish; LB=largemouth bass; SG=spotted gar; YB=yellow bullhead.
[c]2,3,7,8-tetrachlorodibenzo-*p*-dioxin
[d]2,3,7,8-tetrachlorodibenzofuran
[e]All tetra-, penta-, hexa, hepta, and octo-dioxins and furans

edema and hemorrhaging due to exposure to extremely low (ppt) concentrations of TCDD and structurally related congeners. Fin necrosis, lesions, induction of cytochrome P450, histopathological changes and suppression of the immune system are among the responses noted in fish exposed to a lethal concentration (100 ppt; U.S. Environmental Protection Agency 1993).

One hundred-percent mortality of avian embryos has been reported at levels of exposure equal to a dietary fish concentration of 3 to 14 pg TCDD/g (ppt) of tissue (U.S. Environmental Protection Agency 1993); essentially the same range of concentrations noted in fish collected during this present study.

Male rats, exposed to TCDD either *in utero* or via lactation, displayed a reduction in anogenital distance, delayed descent of testis, and reduced weight of testis, epididymis and accessory sex organs (Peterson et al. 1992). Peterson et al. (1992) also reported inhibited spermatogenesis, demasculinized and feminized sexual behavior and an alteration in the regulation of luteinizing hormone (LH) secretion. However, mink (*Mustela vison*) appear to be one of the most sensitive mammalian species. Dietary levels of 0.5 to 1.0 pg TCDD/g (ppt) of tissue has been determined to the threshold level for this species (U.S. Environmental Protection Agency 1993). All fish concentrations were above these levels.

Although not above the FDA guideline (20 ppt), the TCDD concentration in spotted gar tissue from Mercer Bayou in the WMA (site 39) exceeded the current predator protection limit (Table 4). However, it should be noted that much lower numbers for permissible environmental concentrations (with respect to protection of fish-eating species, including humans) of TCDD are currently being reviewed by the EPA. If accepted, most of the concentrations noted in this report will exceed the new PPL.

Metals

With the exception of boron and cadmium, metal concentrations found in sediment samples are reported in Table 10. Boron was detected only in sediments from the following locations: Days Creek at Stateline Bridge (site 9); Days Creek below Texarkana Wood Preservative (site 26); the east side of the Western Refuse landfill (site 34); and Mercer Bayou on the WMA (site 39). The concentration at all four locations was 3.0 ppm (detection limit=2.0 ppm). Cadmium was detected only in Mercer Bayou (site 39) sediments at a concentration of 0.5 ppm (detection limit=0.4 ppm).

Many of the metals detected in sediments from the watershed, including arsenic, chromium, copper, lead, nickel and zinc are normal constituents of aluminosilicate clays (Turekian and Wedepohl 1961). Schropp et al. (1990) and Facemire (1991) used aluminum as a reference element to normalize concentrations of these metals in order to determine whether metal concentrations observed in sediments were of natural or anthropogenic origin. Although complete digestion is necessary for accurate analysis, data presented herein appear

Table 10. Metal concentrations (ppm dry weight) detected in sediments from the Sulphur River Watershed - March and August 1990.

							Analyte									
Site	Al	As	Ba	Be	Cr	Cu	Fe	Pb	Mg	Mn	Hg	Ni	Se	Sr	V	Zn
9	2180	1.8	48.3	0.20	5.0	4.4	2460	17.0	167	53.2	0.05	2.0	0.2	5.3	4.9	27.2
19	716	0.68	25.0	<0.10	2.0	1.6	917	5.0	47	19.0	0.02	1.0	0.3	2.0	2.1	8.1
20	2780	14.7	58.8	0.20	5.7	6.4	3520	26.0	200	85.2	0.07	3.0	0.2	5.3	6.3	32.9
25	27300	2.3	158.0	1.6	23.0	11.0	18000	16.0	2330	293	0.04	14.0	0.6	60.4	24.0	79.0
26	1790	1.3	48.5	0.20	4.5	5.1	4180	25.0	145	66.1	0.05	2.0	0.3	4.2	5.2	33.9
27	2380	0.91	49.1	0.20	3.7	2.3	3060	10.0	221	120	<0.01	3.0	0.3	6.5	4.9	18.0
28	1770	1.3	59.1	0.10	3.9	1.4	3200	5.0	109	65.6	<0.01	2.0	0.77	5.3	7.2	7.8
29	5600	4.1	74.8	0.33	8.1	6.2	5700	21.0	329	204	0.07	4.0	0.4	9.0	9.2	38.0
31	16800	3.8	134.0	0.67	20.0	9.8	27800	10.0	1550	86.8	0.09	10.0	0.74	12.6	26.0	31.6
32	12800	3.4	97.1	0.60	14.0	7.7	17800	8.0	1660	209	0.03	9.7	0.5	9.8	18.0	27.2
33	8000	1.7	77.7	0.37	9.9	4.2	9050	6.0	908	77.0	0.03	7.9	0.3	8.9	12.0	15.0
34	2840	0.94	35.9	0.20	5.1	2.1	2770	4.0	171	41.9	<0.01	3.0	0.3	6.3	6.6	7.6
36	13300	2.4	85.8	0.62	13.0	5.6	11100	8.0	1010	92.7	0.03	7.5	0.4	9.5	17.0	21.0
38	2970	1.2	54.5	0.29	8.2	1.9	3650	5.0	182	74.6	<0.01	3.0	<0.2	6.9	7.4	7.6
39	31200	5.2	228.0	1.6	27.0	19.0	20600	22.0	4400	673	0.09	25.0	0.65	81.3	31.0	93.0

to indicate that metal concentrations at some sites were above those normally associated with alumino-silicate clays. These elevated concentrations, if real, are due to human input. However, all metal concentrations in sediments were less than the appropriate level of concern.

Mercury. Metals were detected in all fish tissue samples (Table 11). Of those analytes listed in Table 11, the FDA has established a guideline only for mercury (Table 4). Mercury is one of few metals that bioaccumulates and biomagnifies in the food chain. In fish and wildlife species, mercury is carcinogenic, mutagenic, and teratogenic. In addition, mercury is easily transformed by bacteria from the less toxic, inorganic form to the more toxic, organic form (monomethylmercury) which is more readily absorbed into fish and wildlife tissue (Eisler 1987b).

Some states have chosen a limit for mercury in food for human consumption <1.0 ppm. For example, Florida posts a limited fish consumption advisory when the mercury concentration in filets exceeds 0.5 ppm. With the exception of spotted gar from Mercer Bayou (site 39), all fish samples contained less than this level.

Eight of ten samples contained concentrations of mercury above the PPL (Table 4) and the national mean concentration (0.1 ppm; Schmitt and Brumbaugh 1990). Elevated concentrations of mercury were found in sunfish from Days Creek below Texarkana Wood Preservative (site 12); largemouth bass, spotted gar, and channel catfish tissue from Baker Slough below International Paper (site 25); yellow bullhead tissue from Days Creek below the landfill (site 22) and from Days Creek downstream of Kerr-McGee (site 29); and bowfin and spotted gar collected in Mercer Bayou (site 39). Thus, fish-eating mammals and birds, in addition to carnivorous species of fish, may be at risk.

Mercury contamination resulted in decreased reproductive success of bald eagles (Wiemeyer et al. 1984) and mallards (Heinz 1979), and altered behavior (Heinz 1975, 1979) and brain lesions (Heinz and Locke 1976) in mallards. Roelke et al. (1991) reported reproductive impairment and mortality of Florida panthers (*Felis concolor coryii*) due to chronic exposure to mercury via the aquatic food chain.

Chromium. Chromium concentrations were 1.5 to more than 10 times the PPL in all samples. Chromium, particularly in the hexavalent form (Cr^{+6}), is a mutagen, teratogen, and carcinogen (Eisler 1986c). No biomagnification has been observed in the food chain, and concentrations are usually highest at the lowest tropic levels (Eisler 1986c). The FDA has not established a legal limit for chromium in fish and fish products for human consumption; however, Hong Kong has a legal limit of 1.0 ppm (U.S. Environmental Protection Agency 1989). Spotted gar tissue from Baker Slough and Mercer Bayou on the WMA (sites 25 and 39, respectively) and yellow bullhead from Nix Creek (site 28) contained chromium concentrations that exceeded this limit. As all samples contained

Table 11. Metal concentrations (ppm wet weight) detected in fish collected from the Sulphur River watershed - July 1991.

	Sample Identification[a]									
Analyte	SF12	SF13	YB22	LB25	SG25	CC25	YB28	YB29	BF39	SG39
Arsenic	0.02	0.02	0.04	0.13	0.08	0.064	0.02	0.02	0.15	0.07
Cadmium	0.037	0.027	0.028	-[a]	0.008	-	0.056	0.056	-	0.077
Chromium	0.68	0.99	0.34	0.31	3.1	0.51	0.36	2.1	0.74	2.3
Copper	1.2	0.30	0.62	0.52	0.41	0.34	0.66	0.69	1.4	0.36
Lead	0.58	0.96	-	-	0.30	-	0.20	0.20	-	0.20
Mercury	0.317	0.090	0.200	0.370	0.407	0.180	0.078	0.200	0.200	0.510
Nickel	0.34	0.63	0.36	0.34	3.0	.034	1.3	.036	.051	3.1
Selenium	0.39	0.63	0.28	0.34	0.20	0.26	0.33	0.28	0.27	0.2
Vanadium	-	-	-	-	-	0.19	0.10	-	-	0.34
Zinc	22.7	26.2	13.5	12.6	20.5	16.8	21.7	13.5	11.6	19.7

[a]Below detection limit. Detection limits were: cadmium=0.008; arsenic, chromium=0.02; copper, nickel, selenium, zinc=0.04; lead, vanadium=0.1.

chromium levels greater than the PPL, it is possible that sensitive freshwater aquatic species have suffered adverse impacts including reduced growth and inhibited reproduction as reported by Eisler (1986c).

Copper. No PPL could be found for copper, but concentrations in sunfish from Days Creek south of Texarkana Wood Preservative (site 12) and bowfin tissue from Mercer Bayou (site 39) were greater than the 85th percentile (0.9 ppm) for all fish collected during an NCBP survey (Lowe et al. 1985). Although copper is a toxic pollutant pursuant to section 307(a)(1) of the Clean Water Act and is listed by the EPA as one of 129 priority pollutants (Keith and Telliard 1979), the FDA has not established any criterion protective of human health. Venezuela has set a legal limit of 10 ppm for copper in fish products (Pastorok 1987). All fish samples from the watershed contained copper concentrations below this limit.

Lead. Lead concentrations exceeded both the recommended edible tissue level and the PPL (Table 4) in sunfish from Days Creek below Texarkana Wood Preservative (site 12) and Nix Creek (site 13), and equalled the PPL in spotted gar collected from Baker Slough downstream of the International Paper effluent outfall (site 25).

All measured effects of lead on living organisms are adverse (Eisler 1988a). Ames et al. (1987) stated that some salts of this element are carcinogenic. Effects of sublethal concentrations of lead include increased mucous formation, delayed embryonic development, suppressed reproduction, inhibition of growth, and fin erosion in fish (Rompala et al. 1984).

In birds, lead has been implicated in decreases in eggshell thickness, growth, ovulation, and spermatogenesis. Lead concentrations in all samples exceeded the National mean concentration of 0.17 ppm reported by Schmitt and Brumbaugh (1990).

Nickel. No PPL was found for nickel. However, Irwin (1991) reported a background level of 0.9 ppm. Concentrations exceeded this level in spotted gar tissue from Baker Slough and Mercer Bayou in the WMA (sites 25 and 39, respectively) and in the yellow bullhead sample from Nix Creek (site 28), but were well below background in the other samples.

Nickel, listed by the EPA as one of 129 priority pollutants (Keith and Telliard 1979), is considered to be one of the 14 most noxious metals (Jenkins 1981) and is also listed among the 25 hazardous substances thought to pose the most significant potential threat to human health at superfund sites (U.S. Department of Health and Human Services 1987, U.S. Environmental Protection Agency 1987). Little information is available on the effects of this element on fish and wildlife species; however, nickel has induced cancer in laboratory animals (U.S. Environmental Protection Agency 1980). Mixtures of nickel, copper, and zinc produced additive toxic effects on rainbow trout (Rompala et al. 1984).

Currently, there is no FDA action level or predator protection limit for nickel in fish flesh.

Selenium. Selenium concentrations exceeded the PPL and the National mean concentration of 0.47 ppm (Schmitt and Brumbaugh 1990) only in the mixed sunfish sample collected from Nix Creek (site 13). Other samples contained selenium concentrations well below the PPL. Thus, selenium is not likely to pose any significant threat in the watershed.

Zinc. When compared to the National mean concentration of 21.7 ppm (Schmitt and Brumbaugh 1990), zinc was slightly elevated only in sunfish from Days and Nix Creeks (sites 12 and 13) and was equal to the mean concentration in yellow bullhead from Days Creek along Stateline Road (site 29). Zinc is an essential element for plants and animals (Keller 1988). However, too much zinc is toxic to humans, fish, and wildlife, and may interact synergistically with copper and ammonia to produce an increased toxic effect to fish (Herbert and Vandyke 1964). There are no established limits for zinc in fish and fishery products in the United States. Concentrations of arsenic, cadmium, and vanadium in all samples were below the respective PPLs (Table 4).

Summary and Conclusions

Microtox™ bioassays indicated biologically toxic soil and sediments on both the north and south side of the Western Refuse landfill. However, the chemicals responsible for the toxicity were not identified. Elevated concentrations of organochlorines, PAHs, TCDD, and various metallic elements in some fish and sediment samples indicate that fish and wildlife species in the Sulphur River watershed and WMA may be at risk. The source of elevated concentrations of *p,p'*-DDE in fish and sediment samples from Baker Slough and the WMA is likely runoff and soil erosion from agricultural land. The use of DDT was banned by the EPA in 1972. As a result, it is expected that *p,p'*-DDE concentrations in sediments and fish tissues from these areas should decrease over time. Elevated *p,p'*-DDE concentrations in sediments from the Western Refuse landfill may derive from pesticide containers in the landfill.

Sources of PCBs appeared to be Texarkana Wood Preservative and the Western Refuse landfill in Days Creek, and International Paper in Baker Slough. The fact that PCBs were detected only in sediments from near the landfill, but in fish from several other areas, is indicative of the value of using fish to detect the presence of lipophilic compounds. In addition, there appears to be a major source of PCBs upstream of sites 13 and 28 in Nix Creek.

The highest concentration of both carcinogenic and total PAHs were detected in sediments collected in Wagner Creek adjacent to the Koppers superfund site and Stateline bridge. Koppers Superfund site and the operational

Kerr-McGee site are believed to be the major sources of PAHs within the watershed.

Although elevated concentrations of TCDD were detected in fish in Days Creek below the Western Refuse landfill, which is likely a source of TCDD contamination, the major source for TCDD in the watershed is the International Paper pulp mill located on Baker Slough. This conclusion is supported by the fact that dioxins and furans are common constituents in pulp mill effluents and that these contaminants were not detected in the Sulphur River above the paper mill.

Mercury concentrations in fish tissues were greatest in Days Creek below Texarkana Wood Preservative, in Baker Slough downstream of International Paper, and in the WMA. However, although both facilities appear to be sources of mercury contamination in the watershed, one must be cautious in making this assumption. Mercury concentrations in fish from other locations were measured in either sunfish or catfish, which typically contain less mercury/g body weight than top predators such as largemouth bass and spotted gar (Facemire, unpublished data). Thus, valid between-site comparisons may be made only when fish from each site are of the same species, size and age.

Lead and chromium, detected at elevated concentrations in fish samples, are perhaps most important in terms of potential impact to fish and wildlife resources. Lead concentrations were greatest in Days Creek below the Texarkana Wood Preservative site and in Nix Creek just above the confluence of that stream with Days Creek.

Chromium may or may not be a problem. Typically, hexavalent chromium is the most toxic form; but, the trivalent form is most commonly found. As speciation of chromium was not completed in Sulfur River watershed samples, information relative to the form present in the fish of the Sulphur River watershed would be required before we can determine the risk to fish and wildlife resources in the watershed and WMA. It should be noted that chromium levels seemed to be those one would expect given the amount of aluminum present in the sediments sampled. Thus, the source of this metal may be the sediments themselves. Further studies would be necessary to accurately identify the sources of both lead and chromium.

8. A variety of techniques should be employed to monitor contaminant impacts in the Texarkana area on an annual basis. We recommend the following paradigm:

a. **Use Microtox^{TM} bioassays to screen for toxic sediments and pore water.**

b. **For those samples found to be toxic, conduct:**

- **acute and chronic toxicity tests of pore water using *Ceriodaphnia* sp.;**

- **acute toxicity tests of pore water using fathead minnows**
- **acute toxicity tests of sediments using *Hyallela azteca*, *Chironomus tentans* or *C. riparius*.**

c. **Additional *in situ* bioassays should be conducted at sites where confirmed tests indicate toxic sediments.**

Recommendations

To protect fish and wildlife resources of the Sulphur River watershed and WMA, the following measures are recommended (not in priority order):

1. **The Arkansas Department of Pollution Control and Ecology and the Arkansas Game and Fish Commission should conduct additional biomonitoring or contaminant investigations of the landfill and adjacent areas to determine which chemicals are responsible for the toxicity noted by Microtox™ bioassays.**

2. **The source(s) of PCBs in Days Creek must be determined and further releases should be prevented; and, if, upon further investigation, fish and wildlife resources are found to have been adversely impacted by PCBs in sediments, contaminated sediments should be removed.**

3. **The EPA should be requested to investigate the feasibility and responsibility of cleaning up contaminated stream reaches associated with the sites having elevated levels of PAHs. Elevated levels of PAHs have likely resulted in injury to trust resources. This must be determined and, if so, the Service should consider a claim for damages.**

4. **Dioxin concentrations in sediments and fish should be monitored annually upstream and downstream of the paper mill effluent outfall and in the WMA. If it is determined that dioxin is present at undesirable levels in fish tissues, the Texas Water Commission should take action to reduce the dioxin discharged from the paper mill.**

5. **The extent and severity of mercury contamination in the watershed should be determined.**

6. **The source of PCBs and other contaminants in Nix Creek should be determined.**

7. **Annual fish collections should be made from the Sulphur River WMA and watershed to monitor levels of OCs, PAHs, dioxins, furans, and metals. The Texas Water Commission should investigate elevated concentrations of PAHs in runoff from the Kerr-McGee wood treatment facility and investigate the need, feasibility, and responsibility for cleaning up the contaminated areas of Days Creek.**

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Appendix A

Analytical Methods

Analytical Methods

In addition to the sediment samples found to be toxic by Microtox, several sediment samples not found to be toxic by the analysis were sent to laboratories to be analyzed for metals, dioxins, polycyclic aromatic hydrocarbons (PAHs), and organochlorines (OCs). Analyses of the sediment samples and fish tissues for metals were performed by the Environmental Trace Substances Research Center (ETSRC) in Columbia, Missouri.

After homogenization of the sediment samples, six aliquots of each sample were weighed and frozen. Four aliquots of each sample were retained for metal analysis (one each for mercury, selenium, arsenic, and inductively coupled plasma emission spectroscopy (ICP) analysis for the remaining metals). The two remaining aliquots of each sample were sent to the National Fisheries Contaminant Research Center (NFCRC) and the Geochemical and Environmental Research Group (GERG), College Station, Texas, for dioxin, and PAH and OC analyses, respectively.

All fish tissue samples were processed for analysis by GERG. Samples were homogenized and six aliquots of each sample weighed and frozen creating six sets of samples. The GERG kept one set of samples for OC/PAH analyses, sent four sets to ETSRC for metal analyses (as noted above), and one set to the NFCRC for TCDD and furan analyses.

Samples retained by the ETSRC were freeze-dried, weighed and further homogenized using a Spex Industries, Inc. Model 8000 mixer/mill with tungsten-carbide vial and balls.

Aliquots for mercury analyses were weighed into a freshly cleaned 50 ml round bottom flask. Five ml of concentrated sub-boiled HNO_3 were added and the flask was placed under a 30 cm water-cooled condenser. Heat was adjusted to allow the HNO_3 to reflux no more than one third the height of the column. After 2 h, the heat was turned off and the samples allowed to cool. Condensers were rinsed with 1% v/v HCl and the flasks removed. Samples were diluted with 1% v/v HCL in a 50 ml volumetric flask and then transferred to clean, labeled, 60 ml flint glass bottles for quantification of residues by cold vapor atomic absorption.

Samples to be analyzed for selenium were weighed into a freshly cleaned 100 ml quartz Kjeldahl flask. Fifteen ml of concentrated sub-boiled HNO_3 and 2.5 ml of concentrated sub-boiled $HClO_4$ were added. To control foaming, flasks were placed in a beaker of cold water. After subsidence of the initial reaction, samples were placed on low heat until the evolution of dark red fumes had ceased. Gradually, the heat was increased until the HNO_3 began to reflux. Samples were allowed to reflux overnight, then the heat was gradually increased until the HNO_3 had been driven off, and the reaction with $HClO_4$ began. When dense white fumes from the $HClO_4$ were evident, samples were removed from the heat, allowed to cool, and 2 ml of concentrated sub-boiled HCl were added. Flasks were reheated until containers were hot to the touch or started to boil. Thee heat source was removed and 5-10 ml of deionized water were added.

When cool, each sample was further diluted with deionized water and transferred to clean, labeled, 60 ml polyethylene bottles for quantification of selenium residues by hydride generation accessory. The same digestion procedure was used for arsenic and ICP analyses.

At GERG, freeze-dried sediment and fish tissue samples were homogenized and placed in extraction thimbles. Surrogate standards and methylene chloride were added to sediment samples and these samples were extracted for 12 h. Extracts were treated with copper to remove sulfur and were purified by silica/alumina column chromatography to isolate the OC/PAH fractions. Quantitative analyses were performed by capillary gas chromatography with electron capture detection for OCs, and using a mass spectrometer in the SIM mode for PAHs.

Fish tissue samples were extracted by adding surrogate standards, Na_2SO_4, and methylene chloride in a centrifuge tube. Tissue extracts were purified by silica/alumina column chromatography to isolate the OC/PAH fractions. These fractions were further purified using high performance liquid chromatography (HPLC) to remove interfering lipids. Residues were quantified by capillary GC with electron capture detector for OCs and a MS in the SIM mode for PAHs.

Dioxin and furan analyses were conducted by NFCRC using the following procedure. Sediment and fish tissue samples were frozen awaiting analysis; then air dried, weighed, and blended with a volume of anhydrous sodium sulfate equal to 4x to 5x times their weight. A 50 g portion of each sample was spiked with 600 pg of ^{13}C-labelled polychlorinated dibenzofurans and dibenzo-*p*-dioxins. Extractions for all samples were performed in 1.5 cm i.d. glass columns using 250 ml of methylene chloride for each 30 g of sample. Control materials, spiked sediments, and matrix blanks were processed concurrently with samples. Sample extracts were enriched using sulfuric acid treated silica gel with potassium silicate and silica gel, copper treatment for sulfur removal, and elution on a carbon column and an alumina column. Sample fractions were individually transferred to autosampler vial inserts and concentrated to less than 10 μl with nitrogen. An instrumental internal standard, ^{13}C-labelled 1,2,3,4-PCDD, was added to each vial before gas chromatography-mass spectrometry (GC-MS) analysis. A VG 70-250S capillary GC/high resolution MS operating at 10,000 resolution was used to quantify the residues of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) and 2,3,7,8-tetrachlorodibenzofuran (TCDF) in the sediment samples.